

REQUEST FOR RECONSIDERATION

Claims 1-21 are active in the present application. Claims 2 and 8-20 are presently withdrawn from prosecution. Claims 1, 3-7 and 21 are currently under active prosecution.

Present independent Claim 1 contains the following limitation among others:

a pretilt angle in each of the liquid crystal anchoring direction with respect to the corresponding substrate surface is substantially zero.

It appears that it is the Office's position that the prior art cited against the present claims discloses a liquid crystal device having liquid crystal anchoring directions each of which as a pretilt angle of substantially zero. On page 6 of the Office Action of May 18, 2005, the Office states the following:

Kim discloses a liquid crystal device wherein the pretilt angle in each of the plurality of liquid crystal anchoring direction with respect to the corresponding substrate surface is substantially zero when the photo energy more than 6000 mJ/cm (Fig. 4, col. 5 lines 30-32) or less than 5° that is in a range 0-5° (col. 1 line 35-36).

The Office cites to Figure 4; column 5, lines 30-32; and column 1, line 35-36 of Kim (U.S. 6,091,471) as support that the prior art patent discloses the above-mentioned limitation of the present claims. Figure 4 of Kim is described as follows in the prior art patent:

FIG. 4 is a graph illustrating the relationship between the photo-energy of ultraviolet light and the pretilt angle of the photo-aligned layer formed with polysiloxane based materials. (Column 3, lines 51-54).

Figure 4 of Kim therefore shows only that one particular photo-aligned layer formed from one particular material (i.e., a polysiloxane) may have a pretilt angle that approaches zero. Kim does not disclose a liquid crystal display device having a plurality of anchoring directions wherein each of the alignment layers has a pretilt angle of substantially zero. The description of Kim at column 5, lines 30-32 cited by the Office merely puts the disclosure of Figure 4 in textual form. It does not disclose a liquid crystal device having an alignment

layer having a plurality of in-plane anchoring directions each of which has a pretilt angle of substantially zero.

The Office cited to column 1, lines 35-36 as further support for the rejection. The relevant text is reproduced below for convenience.

The liquid crystal cell is classified a vertical aligned liquid crystal cell and a horizontal aligned liquid crystal cell depending upon the pretilt angle. The vertical aligned liquid crystal cell typically defines a liquid crystal cell having a pretilt angle of an alignment layer larger than 60°, the horizontal aligned liquid crystal cell typically refers to a liquid crystal cell having a pretilt angle of an alignment layer less than 5°. (Column 1, lines 29-37).

The above-quoted disclosure of Kim is merely a general definition of the conventional terms “vertical aligned liquid crystal cell” and “horizontal aligned liquid crystal cell”. The description cited by the Office does not disclose a liquid crystal device having a plurality of in-plane anchoring directions each of which has a pretilt angle that is substantially zero. As Applicants have stated above, Kim does not disclose a liquid crystal display device having a plurality of anchoring directions wherein each anchoring direction has a pretilt angle of substantially zero.

Kim discloses liquid crystal cells that contain first and second alignment layers. Kim discloses the prior art method and device as follows:

An object of the present invention is to provide a liquid crystal cell having an alignment stability and a wider viewing angle by simplifying the process and the fabrication method thereof.

To achieve the object mentioned above, the method for fabricating the liquid crystal cell of the present invention comprises the following steps of: providing a first alignment layer on a first substrate; **rubbing** said first alignment layer such that said first alignment layer has a first pretilt angle associated therewith; providing a second alignment layer on a second substrate; exposing said second alignment layer to light such that said second alignment layer has at least one second pretilt angle associated therewith; and providing a liquid crystal material between said first and second substrates. (Column 2, line 64 through column 3, line 7).

Thus any liquid crystal display device of Kim must contain at least an alignment layer that is prepared by rubbing. Applicants submit that it is generally recognized by those of skill in the art that rubbing cannot provide an alignment layer wherein the pretilt angle is substantially zero. Applicants submit herewith copies of Geary et. al., *J. Appl. Phys.*, 62, 4100, 1987 and Seo et. al., *Jpn. J. Appl. Phys.*, 34 L503, 1995. Geary et. al. discloses, for example, in section II and in Figure 1(c) that a tilt bias is generated by buffing (e.g., rubbing treatment). See for example the disclosure on page 4101 first full paragraph left column and Figures 1(A)-(D).

Seo et. al. discloses in section 3 that a pretilt angle (i.e., θ_0) is generated by rubbing. In fact, Seo et. al. discloses that a polymer surface may have a tilt angle of 0° before rubbing (e.g., when rubbing strength RS is 0). But after rubbing a pretilt angle θ_0 arises (see Figure 5 (A)-(B)).

Applicants submit that Geary and Seo demonstrate that it is known that rubbing treatment does not provide a pretilt angle of substantially zero and that rubbing treatment instead is known to result in a tilt bias in aligned liquid crystal systems.

Kim discloses an invention that must have a layer prepared by rubbing. It is not possible for the pretilt angle of each liquid crystal anchoring direction of the liquid crystal cell of Kim to be substantially zero because such rubbing cannot provide an anchoring direction having a pretilt angle that is substantially zero. Applicants submit that Kim cannot anticipate the present claims because Kim does not explicitly, implicitly or inherently disclose at least one limitation of the presently claimed invention.

Applicants further submit that Kim actually teaches away from the claimed invention. At column 2, Kim discloses that small pretilt angles are disfavored:

However, the photo-alignment method has problems that the process is complicated due to the double exposure and the pretilt angle is too small, for example, the obtained pretilt angles being approximately 0.15° , 0.26° and 0.30° respectively

when the oblique irradiation angles are 30°, 45° and 60°. In addition, it takes long time to irradiate light into the alignment layer so total tact time is prolonged, as well, the alignment stability of photo-alignment method is weaker than that of rubbing method. (Column 2, lines 49-57).

Kim teaches away from the use of a photo-alignment method as evidenced by the prior art disclosure that “the pretilt angle is too small” under photo-alignment conditions. Applicants submit that Kim’s disclosure that small pretilt angles are disfavored is directly contradictory to the present claim limitation that the pretilt angle of each liquid crystal anchoring direction of the present claims must be substantially zero (e.g., contrary to Kim’s disclosure that pretilt angles of, for example, 0.15° are “too small”).

Applicants submit that Kim teaches away from the presently claimed invention by stating that pretilt angles of as much as 0.6° are too small. Applicants submit that the Office’s assertion that Kim may encompass low pretilt angles (e.g., pretilt angles that are less than 5°) is not sufficient evidence from which to determine that the claimed invention is obvious in view of Kim’s disclosure that low pretilt angles are a problem.

In regard to the Office’s reliance of the prior art’s Figures as evidence of obviousness, Applicants submit that Figure 14 of Kim shows a projection of the prior art anchoring direction onto the plane defining the liquid crystal display. Thus the arrows present in the plane of Figure 14 do not indicate that the anchoring direction is perfectly horizontal (e.g., have a pretilt angle of zero degrees); instead, the arrows show the projection of the anchoring direction on a two-dimensional plane.

The pretilt angles of Kim are also shown in Figures 5, 6, and 11-13. These figures include a side view that shows angled lines at the top of a display device. Applicants submit that the angle of the lines represents the pretilt angle. Because the angles are different and not directly perpendicular or parallel to the device, not all of the pretilt angles of the prior art liquid crystal display device are zero.

Figure 14 shows an embodiment where the prior art device is made up of four domains (e.g., the squares of the pattern). Each of the squares of the prior art Figure 14 has a distinct pretilt angle. The benefit of the multi-domain multi-angle device of Kim is a wider viewing angle. Kim discloses, for example:

To overcome said problems, a multi-domain TNLC cell such as a two-domain liquid crystal cell, and a four-domain liquid crystal cell is introduced. The multi-domain liquid crystal cell has a wider viewing angle by providing more than domains in each pixel, domains having different pretilts with respect to each other, so as to compensate the viewing angle dependence of each domain. (see column 1, lines 59-65).

Thus it is explicitly disclosed in Kim that the prior art domains have different pretilts. Because the pretilt angles of the domains of Kim are different they cannot all be substantially equal to zero.

This points to a basic difference between Kim and the presently claimed invention. The structure of Kim has different pretilt angles in different domains to achieve a wide viewing angle. In contrast, the claimed invention has pretilt angles that are substantially equal to zero (i.e., see Claim 1 where it is stated “a pretilt angle in each of the liquid crystal anchoring directions with respect to the corresponding substrate surface is substantially zero”).

Moreover, Applicants submit that the multi-domain checkerboard architecture of Kim is necessarily of completely different scale than an embodiment of the invention having a checkerboard pattern. The pattern of the invention is a few microns to sub-micron in scale or else the bistable states of the liquid crystals of the claimed invention cannot be realized. The domains of Kim are more than 10 μm in scale or else it would not be possible to achieve the wide viewing angle desired in the prior art device.

Further with regard to the wide viewing angle of Kim, Applicants submit that if the prior art were to have a pretilt angle of substantially zero the quality of the prior art display

device would drop significantly because the prior art pixels would have a granularity that would prevent a wide viewing angle.

In response to the arguments filed by Applicants on November 8, 2004, the Office remarked that Kim discloses a device capable of maintaining a plurality of stable in-plane alignment states even after removal of the applied electric field (e.g., the domains in the OFF state in Figure 10a and Figure 14a-j) and thereby form a plurality of liquid crystal in-plane anchoring directions (see the Response to Arguments section on page 6 of the Office Action of May 18, 2005). Figure 10a of Kim discloses the in-plane switching mode. The two stable alignment states recited in the present claims can not be achieved in an in-plane switching mode. Thus the assertion that the claimed invention is obvious in view of Kim is further supportable.

Applicants submit that the Office improperly equated the “plurality of stable in-plane alignment states” of the claimed invention with the “plurality of domains” of the prior art. Stable in-plane alignment states are not the same as domains and the Office provided no sound basis for asserting that these two different concepts are the same or that those of skill in the art would combine the teachings of one with the other.

Applicants submit that the subject matter of independent Claim 1 is novel and not obvious in view of Kim and respectfully request the withdrawal of the rejection.

Present independent Claim 2 contains the following limitation, among others:

the device is capable of maintaining two stable in-plane alignment states of the liquid crystal layer even after the removal of the applied electric field.

The Office cites to Figure 10 and 14a-j as support that Kim discloses a device that is capable of maintaining two stable in-plane alignment states after removal of an applied electric field. Applicants submit that Figure 10 does not disclose a stable in-plane alignment state. Instead, Figure 10a (i.e., in an “off” state) discloses that upon application of an electric

field (i.e., the “on” depiction of Figure 10b) the crystal orientation of aligned crystals changes. Whereas in Figure 10a each of the plurality of crystals is aligned in parallel, in Figure 10b the crystals twist relative to one another so that the top crystal is perpendicular to the bottom crystal. There is no disclosure in Kim that the “on” state (e.g., the state where an applied electric field is present) is stable and will not otherwise revert to the “off” state upon removal of the electric field.

Figure 14 of Kim “shows a process for fabricating a four-domain liquid crystal cell” (column 8, lines 42-43). The Office cited to each of Figures 14a-j as support for the rejection of Claim 2. However, many of the embodiments of Figure 14 do not include the application of an electric field. In fact, the substeps depicted in Figure 14 refer only to rubbing and photo-irradiation (see column 8, lines 42-47 reproduced below for convenience):

FIG. 14 shows a process for fabricating a four-domain liquid crystal cell. A two-domain first substrate 1 is prepared by the reverse rubbing, as shown in FIG. 14a, FIG. 14b and FIG. 14c. The Four-domain second substrate 2 is prepared by changing the photo-irradiating direction, as shown in FIG. 14d-FIG. 14i.

Applicants submit that the disclosure of Kim cited by the Office as support for the rejection of the present claims does not disclose a liquid crystal device capable of maintaining two stable in-plane alignment states after removal of an applied electric field. Applicants respectfully request the withdrawal of the rejection.

As noted in the comments above, Applicants submit that the claims of the present application are patentable over the prior art of record and respectfully request the withdrawal of the rejection and allowance of all now-pending claims.

Upon determining that the subject matter of Claims 1 and 2 is allowable, Applicants request the Office expand the search to include the non-elected species and rejoin any claims dependent from allowable Claims 1 and/or 2 where such claims were previously withdrawn on the basis of the Office's Restriction Requirement.

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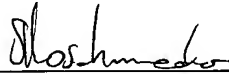
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The mechanism of polymer alignment of liquid-crystal materials

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Smectic and nematic liquid-crystal materials can be homogeneously aligned by buffed thin films of appropriate polymers. We propose that the buffing process orients the polymer's molecular chains in a manner similar to cold drawing of bulk polymer samples. Experimental verification of this theory is obtained by measuring buffing-induced birefringence in thin films of various polymers coated on glass. Further experiments establish that the oriented state of the polymer chains, and not scratching or grooving of the surface, is necessary to produce alignment. Alignment is found to occur when the polymer is both oriented and crystalline. A picture of alignment is presented in which the formation of a liquid-crystal phase on the crystalline, oriented polymer surface is analogous to the epitaxial growth of conventional solid crystals.

I. INTRODUCTION

Homogeneous alignment of liquid-crystal materials can be achieved by coating the surfaces of the cell that is to contain the liquid crystal with a very thin film of a linear polymer which is mechanically rubbed or buffed.^{1,2} In the case of nematic materials, this method provides alignment superior to the weak alignment that can be produced by buffing uncoated surfaces. The method also yields good alignment of smectic materials, which are otherwise very difficult to align by buffing.

It is of considerable practical and theoretical interest to understand the mechanism by which such polymer alignment methods work. Specifically what alteration of the polymer takes place when the surface is rubbed? How does this alteration act to align the liquid-crystal molecules? And, especially in the case of smectics, why do some polymers produce good alignment while others produce no alignment at all?

One possibility is that polymer alignment acts through grooves or scratches induced by the buffing process.^{3,4} While such a mechanism may be applicable to some situations, we find it to be an unsuitable explanation in the case of buffed polymer alignment for two reasons. First, alignment can be produced by buffing with a soft material and using a light pressure, conditions that seem unlikely to produce substantial scratching of the polymer surface. Second, different polymers are observed to differ strikingly in their ability to align. Using electron microscopy, we have found that buffed polymer surfaces can exhibit strong aligning ability and yet show no evidence of scratching or grooving. Even if significant scratching were to occur during buffing, this cannot explain the variation in aligning ability, since we find that the variation is uncorrelated with the mechanical hardness of the polymer.

An alternative concept is that alignment acts through the orientation of polymer molecules. The hypothesis has been advanced by Castellano⁵ that buffing can orient the molecular chains of a polymer coating through localized melting, producing an aligning surface. Others have reported experimental evidence implying that oriented polymer surfaces can act to align liquid-crystal materials. Kondo *et*

*al.*⁶ have described alignment of smectics close to cell spacers made from oriented polymer sheets. Aoyama *et al.*⁷ have reported alignment of nematics in cells whose surfaces were made of stretched polymer films. Aligning ability of dip-coated polymer films along the direction of withdrawal from a polymer solution, without any buffing, has been reported by Becker *et al.*⁸ More recently, Clark⁹ observed surface memory effects on polymer-coated surfaces and attributed them to plastic deformation of the polymer film.

The present article is an experimental investigation of the hypothesis that polymer chain orientation can act to align liquid-crystal materials. There are two physical processes that must be considered: (1) the orientation of the polymer by the buffing process and (2) the interaction of the oriented polymer with the liquid-crystal material to cause alignment. Concerning the first process, a mechanism is proposed through which buffing can produce chain orientation in a thin polymer film in a manner resembling the cold drawing of a bulk polymer sample. The orientation of polymer chains by buffing is experimentally verified by birefringence measurements, and additional experiments are presented which support and clarify the mechanism. The second of the two physical processes is investigated by observing alignment caused by various polymers, both in conventional cells and in cells formed from cold-drawn bulk polymer samples. It is found that crystallinity of the polymer, as well as chain orientation, is necessary for the aligning effect to occur. Finally, an analogy is drawn between the epitaxial growth of conventional solid crystals and the formation of a liquid-crystal phase on the surface of a crystalline, oriented polymer surface.

II. THE BUFFING PROCESS

Buffing of the polymer-coated surface is accomplished by the unidirectional motion of a fibrous material which is pressed into contact with the surface. The fibers of buffing materials are generally a number of micrometers in diameter, while the polymer films used in liquid-crystal alignment are typically 200–300 Å thick. The contact area between fiber and polymer that is created by the buffing pressure, while substantially less than the fiber diameter, can reasona-

bly be expected to be substantially broader than the film's thickness. Hence, during buffing the polymer film is caught between two broad planes, one stationary (the substrate) and the other moving (the fiber contact area). Thus, the polymer will experience a shearing force, and, if the friction exerted by the fiber contact area is great enough, a permanent shearing deformation can result.

The geometry of such a deformation is illustrated in cross section in Fig. 1. A rectangular portion of the film will tend to be sheared into a parallelogram [Fig. 1(b)], a form of deformation equivalent to pure elongation along the principal axes of stress oriented at 45° , as shown. With continued deformation, an extreme parallelogram form [Fig. 1(c)] will be produced. In this state, the axis of elongation, illustrated in the figure, will be nearly parallel to the polymer surface. Thus, through the action of shearing, the polymer film will be deformed much as if it had first been elongated by cold drawing and then placed upon the substrate. The deformed film will differ from this state only in that its axis of elongation will be somewhat inclined with respect to the substrate, to a degree dependent on the extent of deformation.

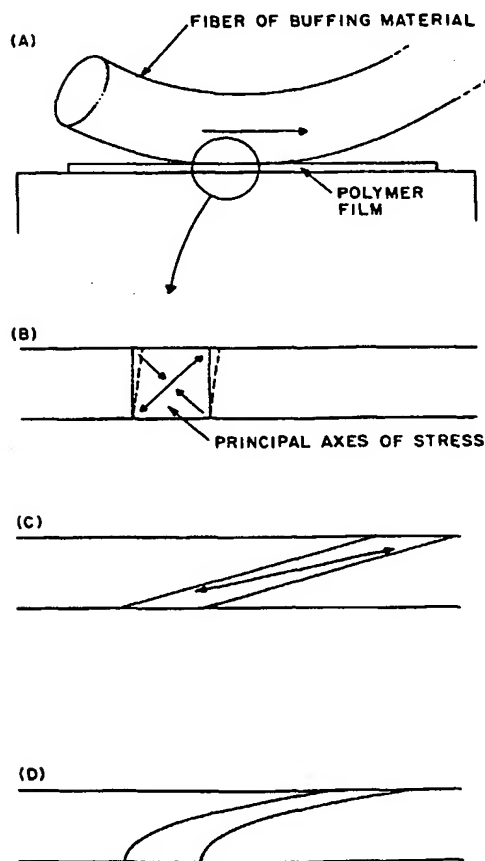


FIG. 1. (a) Cross-section view of a polymer film in contact with a moving fiber of buffing material. (b) Magnified view of the film under shearing forces, showing the principle axes of stress. (c) Effect of large shear deformation, similar to that which would be produced by simple elongation parallel to the substrate. (d) Modified version of large shear deformation, taking into account a possible proximity effect exerted by the substrate surface on the polymer.

The parallelogram form shown in Fig. 1(c) is of course an idealization. The plastic deformation of polymers is complex and may involve both nonlinear and hysteretic effects. This complexity is evident when the cold-drawing behavior of bulk polymer samples is examined. Often the sample "necks down" as it is stretched so that a thin, fully elongated segment is created somewhere along the length of the sample. This segment grows as regions of rapid plastic deformation advance into the undeformed portions of the sample. In polycrystalline samples, the degree of crystallinity increases as a result of the elongation, and the crystallites become oriented. Strongly amorphous polymers sometimes neck down also and can exhibit a directional correlation of their polymer chains while remaining noncrystalline. In the situation of Fig. 1, the deformation process is further complicated by the extreme thinness of the polymer film which makes it likely that surface effects will be significant. Binding of the polymer chains at points where they contact the substrate could lead to deformation like that suggested in Fig. 1(d). Experimental evidence presented in Sec. III C points to such a deformation profile as being more realistic than that of Fig. 1(c).

Whatever the precise form of the shearing deformation produced by the buffing process, there will always be a residual inclination of the elongation axis of the polymer at the surface. This inclination provides a natural explanation for the common observation in nematics that the direction of rub is reflected in a small tilt of the aligned liquid-crystal molecules. Such a "tilt bias" has always been difficult to understand from the viewpoint of a scratching or grooving mechanism of alignment. It is known that when the buffing material moves over the surface to the right, as shown in Fig. 1, the molecules of the liquid crystal will align so as to be tilted up slightly at their right-hand ends. This sense of tilt is the same as the sense of tilt of the orientation axis of the polymer in the figure. We feel that this correspondence between polymer orientation and liquid-crystal alignment with regard to both existence and sense of tilt tends to support the picture of buffing-induced deformation presented in Fig. 1. We will examine this point further in Sec. III D.

III. EXPERIMENTAL OBSERVATION OF POLYMER CHAIN ORIENTATION

In the above section, the hypothesis of buffing-induced polymer chain orientation has been described. In this section, experimental evidence supporting this hypothesis is presented. Polymer chain orientation is known to induce birefringence. This is a consequence of the difference in refractive index for light polarized parallel to and perpendicular to the polymer chains. Birefringence is induced both by crystalline orientation of the polymer chains and by non-crystalline directional correlation of the chains, as in the case of strongly amorphous polymers. We have employed measurement of birefringence to detect chain orientation that is induced by the buffing process. A number of different polymers were investigated in this manner, and it was found that the effects of buffing correspond in considerable detail to the effects of cold drawing of bulk polymers.

A. Apparatus

Birefringence was measured by means of the apparatus illustrated in Fig. 2. Light from a dc-powered incandescent source passed in sequence through a 633-nm narrow-band filter, a polarizer, a quarter-wave plate, the sample, and a crossed analyzer before reaching a silicon photodiode. The sample consisted of a piece of glass coated with a thin polymer film. During measurement, the sample was held in a fixture that spun around the axis of illumination at a rate of 14 revolutions per second. Under these circumstances, any birefringence in the sample showed up as a 28-Hz variation in the light intensity sensed by the photodiode. This variation was detected by a lock-in amplifier; the reference phase was provided by an optical chopper that constituted the outer rim of the spinning sample holder. The angular orientation of the chopper with respect to the sample was known, so that the direction of the birefringent slow axis could be determined, as well as the magnitude of the birefringent retardation.

The quarter-wave plate in the above apparatus served to increase greatly the amplitude of the intensity variation sensed by the photodiode. With no quarter-wave plate present, the fluctuation of the transmitted light is very small when the sample rotates, displaying a dependence on the retardation of the sample which is quadratic, and varying at four times the rate of sample rotation. With the quarter-wave plate in place, a linear dependence on retardation is seen, yielding a much larger response, at a frequency twice that of sample rotation. It can be shown that retardation θ (in cycles) of the rotating sample can be determined from the rms variation of the photodiode signal, V_{rms} , by

$$\theta = (\sqrt{2}/\pi) (V_{rms}/V_0),$$

where V_0 is the photodiode voltage corresponding to maximum transmitted intensity. The use of the quarter-wave plate permits the direction of the slow birefringent axis to be determined unambiguously by comparison of the phases of the photodiode signal and the chopper reference signal.

B. Measurement procedure

Samples examined with the above apparatus consisted of 2.5×2.5 cm glass plates 1 mm thick (cut from microscope slides) which were coated with a test polymer on one surface. The sample was held in place by a spring clip that exerted a force on the edge of the glass of only 1–2 g. Significantly greater forces were found to induce measurable birefringence in the glass. The sample was square to avoid a similar birefringence due to centrifugal force.

Polymer films were deposited on the glass samples by spinning on dilute (typically 0.5% by weight) polymer solutions and then baking out the solvent. The polymers, their solvents, and the approximate thickness of the resulting films are listed in Table I. Both crystalline and amorphous polymers were chosen so that the effects of crystallinity could be examined. Buffing was performed by pressing the sample down onto a cotton cloth with a weight and moving it unidirectionally over the cloth a fixed distance at a known velocity. The values of pressure and velocity were 7 g/cm^2 and 4 cm/s , respectively. The effects of changing buffing speed were examined, though not extensively. We found no dramatic change in results for buffing speeds from 10 to 0.1 cm/s . A device was employed to move the sample over the cloth so as to produce a repeatable and accurately unidirectional motion over a known distance. The uncoated glass samples exhibited a birefringent retardation of their own. Only glass samples showing initial retardation of 4×10^{-4} cycles or lower were used. Coating the glass with the polymers did not alter this initial value.

The measurement procedure was as follows. An initial measurement of retardation of the polymer-coated sample was made. The sample was then buffed by moving it a given distance over the cloth and the retardation was remeasured. The sample was buffed a second time for a second known distance and the retardation was measured once again. This process was continued, yielding a series of retardation values. The buffing-induced retardation as a function of cumulative buffing distance was then computed as the difference between the initial retardation and the retardation observed after each new increment of buffing. For most of the polymers, the buffing-induced retardation was comparable in magnitude to the retardation of the uncoated glass sample itself, so that no substantial decrease in accuracy resulted from the subtraction of the two readings. The integration time constant of the lock-in was 10 s and integration was allowed to continue for 30 s before a reading was made.

TABLE I. List of spun-on polymer films studied in this article.

Polymer	Solvent	Thickness (Å)
Polyethylene-terephthalate (PET)	Chlorophenol	200–300
Nylon 6/6	Chlorophenol	300–400
Polyvinyl alcohol (PVA)	Water	300
Polyformaldehyde (PF)	Chlorophenol	250
Polystyrene (PS)	Methylethylketone	250
Polycarbonate (PC)	Dichloroethane	250
Polymethylmethacrylate (PMMA)	Methylethylketone	350

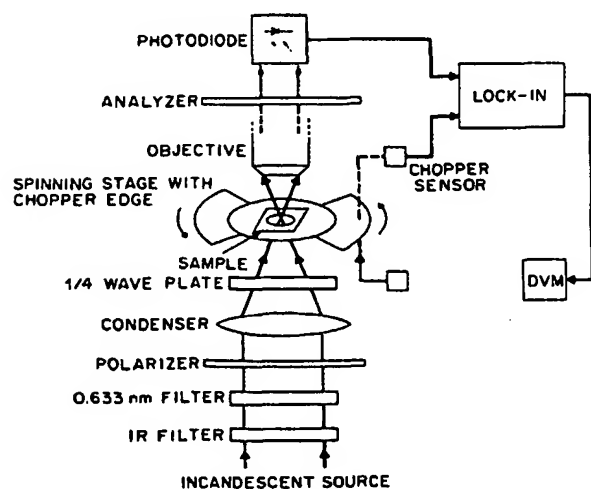


FIG. 2. Apparatus for measurement of birefringence changes of thin polymer films on glass substrates.

Readings made in this way for a given sample were repeatable over a period of several minutes to an accuracy of 1×10^{-3} cycles of retardation.

C. Results

A graph summarizing the observed buffing-induced birefringence for the polymer films studied is seen in Fig. 3. Each curve gives the retardation in cycles averaged over three samples, plotted as a function of the cumulative distance of buffing that each sample had experienced. Both positive and negative values of retardation are plotted, with positive values indicating that the slow axis was parallel to the direction of rubbing and negative ones indicating a slow axis perpendicular to the rub axis. The responses generally show a rapid rise in magnitude of retardation followed by a leveling off. Prominent features seen in the figure are the negative retardation values for polystyrene and the lack of any measurable birefringent response for polymethylmethacrylate. In the remainder of this section, we will examine these and other features of the data of Fig. 3 and shown how they further support the hypothesis of buffing-induced polymer chain orientation.

The negative value of retardation for polystyrene, in contrast with the positive values for all of the other polymers, is perhaps the most striking feature seen in Fig. 3. Drawn bulk sheets of all the polymers were tested for magnitude and sense of birefringence. All could be drawn to some extent; polymethylmethacrylate and polystyrene required warming to allow drawing. All but one of the drawn samples exhibited positive retardation, with the slow axis corresponding to the direction of elongation. The exception was polystyrene, which exhibited a negative retardation. This anomalous bulk behavior of polystyrene is reflected clearly in the negative retardation data for this polymer in Fig. 3. It

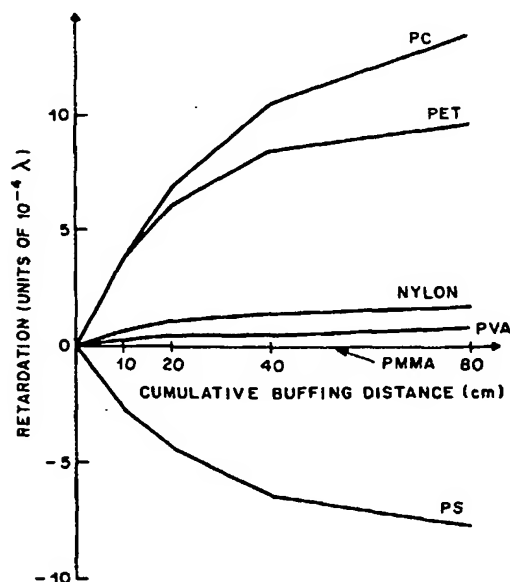


FIG. 3. Plot of retardation induced by buffing. Buffing was performed by pressing the coated sample face down on cotton cloth and pushing it along for a known distance.

is not clear why this material could only be drawn in bulk when warmed, while room-temperature rubbing of a thin film evidently resulted in deformation. Perhaps the substrate exerted a stabilizing effect, preventing fracture, or perhaps some frictional heating of the film occurred during buffing. Nonetheless, the correspondence of negative retardation in both bulk and rubbed film for this material is striking confirmation of the hypothesis of buffing-induced polymer film orientation.

In the case of polymethylmethacrylate, only negligible birefringence could be induced by drawing at elevated temperatures. This very brittle material either deformed as a highly viscous material (when heated) or it fractured. This bulk drawing behavior corresponds well to the data for polymethylmethacrylate in Fig. 3, where no retardation could be observed. Any notion that the retardation measurement technique was actually measuring a spurious effect caused by scratching of the polymer surface during buffing is refuted by the data for this polymer, since polymethylmethacrylate should be as subject to scratches as the rest of the materials.

It will have been noticed that there is no curve in Fig. 3 for polyformaldehyde. The buffing-induced birefringence observed in this material decayed rapidly at room temperature and could actually be seen decaying over the 30-s integration time if the measurement was performed promptly after buffing. It was found that the residual birefringence remaining at room temperature decayed to zero when the sample was heated to 40 °C.

All of the polymers that exhibit a birefringent response to buffing also show a tendency to saturate in their response as the buffing process proceeds. Though no rigidly fixed limit is seen in the curves of Fig. 3, the rate of rise does slow dramatically. This effect is understandable if one considers that the tiny areas of contact between the fibrous buffing material and the polymer film constitute only a minute fraction of the surface's area. As buffing proceeds, these isolated contact areas will leave behind narrow "streaks" of deformation in the polymer film (Fig. 4). At first, the contact areas will encounter only virgin surface, and the fraction of the total area that has been affected by buffing will increase linearly. But as the process continues, the streaks will begin to

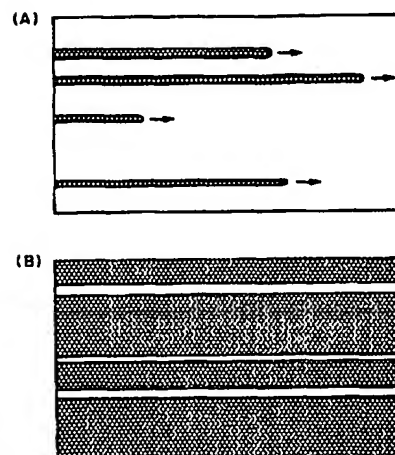


FIG. 4. Accumulation of oriented area of polymer film in streaks as minute regions of contact with the buffing material move across the polymer surface: (a) at beginning of buffing and (b) approaching saturation.

overlap, causing a reduction in the rate at which the buffed area increases. Assuming that most of the deformation that the shearing force at a contact area can cause will occur on first contact, it is then clear that the observed retardation will increase first rapidly, then slow down as more and more of the surface is touched. The plausibility of this streak picture of buffing will be reinforced later in this article.

In Fig. 5, the birefringence, Δn , of the buffed films is plotted against the Δn of the above-mentioned bulk polymer sheets. The maximum retardations recorded in Fig. 3 together with the thickness data of Table I were used to determine Δn for the buffed films. Retardation for the bulk sheets was estimated by fringe counting, observed in 633-nm light, and their thickness was measured with a micrometer after drawing. It can be seen that the Δn for the buffed films is substantially smaller than the Δn for the drawn sheets. It is not clear why the buffed films exhibit smaller birefringence. The reason may relate to the fact that the polymer films are so thin (200–300 Å) that their thickness is substantially less than the length of the polymer molecules themselves. Interactions between the polymer chains and the substrate surface may contribute to an inhibition of chain orientation. For instance, a given chain may come into contact with the substrate surface at a number of points. Any binding to the surface at those points could prevent the full elongation of that chain during buffing. This could give rise to shearing in the polymer layer that was greater near the layer's free surface and smaller near the substrate, as suggested in Fig. 1(d). In spite of the relatively small size of the buffing-induced Δn values, a general trend is evident in Fig. 5, with the materials with large bulk values showing greater film birefringence and those with small bulk values tending to have lesser film birefringence.

D. Further experiments

The above observations indicate that the buffing of thin polymer films induces orientation of the polymer chains in a manner similar to cold drawing of bulk polymer samples. Such orientation offers a straightforward explanation of the birefringence observed. In this section, we describe addi-

tional experiments which support the picture of shearing deformation that was proposed in Sec. II as the mechanism by which buffing could induce such polymer chain orientation.

A key feature of the shearing-deformation theory is the idea of a tilting of the polymer material. This motion transforms a rectangular piece of the film (as seen in cross section) into something like a highly elongated parallelogram, as in Fig. 1. On the basis of this picture, it is natural to conclude that if a polymer film so deformed were buffed in the opposite direction, the process of deformation could be reversed and the magnitude of observed retardation would actually decrease. Such an effect has been observed in polyethyleneterephthalate films. Figure 6 shows birefringence data similar to that of Fig. 3 for a polyethyleneterephthalate film. After 80 cm of buffing in one direction, several additional increments of buffing were performed in the opposite direction. It can be seen that the magnitude of measured retardation decreases significantly, followed by a leveling off. However, if only 10 or 20 cm of buffing in the initial direction were performed, no such decrease was seen.

The above effects of reversed buffing are understandable in light of the "streak" picture of buffing. If only a small amount of initial-direction buffing is performed, then only a minority of the surface's area will consist of streaks of oriented material. Reversed direction buffing will produce new streaks of orientation primarily in untouched areas. No compensation will occur between these two oriented areas, since both represent polymer elongation along essentially the same axis. However, if a surface is thoroughly buffed initially, almost all of its surface will be oriented. During reversed buffing, the tiny areas of contact between the surface and the buffing material will now be likely to overlap with previously oriented material. With overlap occurring, the reversed buffing can act either to reduce the tilted deformation of film or to reverse its direction. In Fig. 6, reduction of tilt seems to occur at first, with consequent lowering of retardation magnitude. Evidently, as reversed buffing continues, actual reversal of the direction of sheared deformation begins to occur so that as old areas of tilt are lost, new ones of equal and opposite tilt are generated. These both contribute equally to retardation, explaining the leveling off seen in the curves of Fig. 3. All of this seems to confirm both the concept of shear

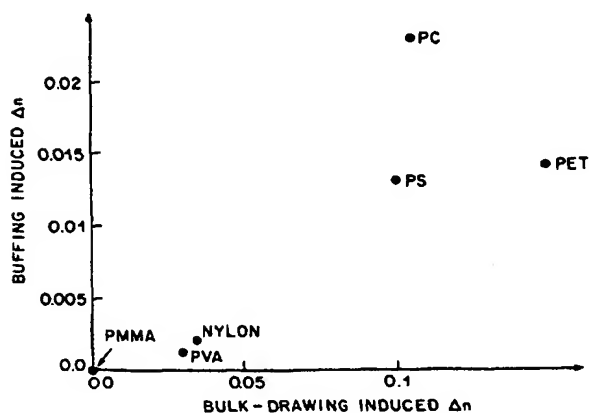


FIG. 5. Plot of magnitude of Δn measured from buffed polymer films vs magnitude of Δn measured from drawn bulk samples of the same polymers. The abbreviations for the polymers are the same as those given in Table I.

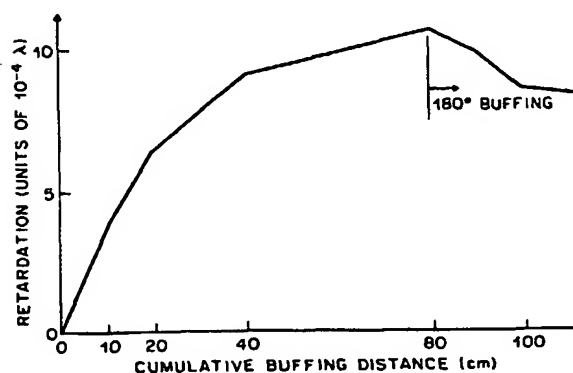


FIG. 6. Plot of retardation of a PET film buffed first in one direction and then in the opposite direction.

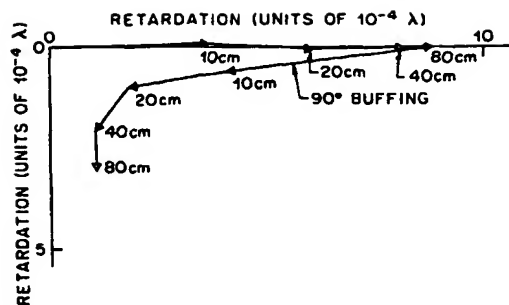


FIG. 7. Polar plot showing magnitude and direction of the slow axis of birefringence of a PET film buffed first in one direction and then at 90° to that direction. Both axes are labeled with the radial scale factor for retardation magnitude. There is no sense associated with the slow axis; the sense of the plotted points was chosen arbitrarily for convenience of display.

deformation induced by buffing and the idea that this deformation occurs by the accumulation of individual streaks caused by the motion of minute areas of contact between surface and the buffing material.

A second experiment, also involving rebuffing of the polymer surface, was performed. A surface coated with polyethyleneterephthalate was initially buffed in a given direction and then buffed at 90° to that direction. The results of this experiment are seen in the plot of Fig. 7. The plot shows in polar form the magnitude of the measured retardation and the angular orientation of its slow axis. (There is no sense associated with this axis and the sense of the plotted points in Fig. 7 was chosen arbitrarily. The sequence in which the data points were taken is indicated by arrows.) It can be seen that the birefringence that accumulated in the initial buffing decreases nearly to zero, followed by a renewed accumulation along the new buffing axis. Some skewing of the birefringent axis toward the direction of initial buffing remains, about 19°.

These results are also understandable in terms of the picture of polymer deformation developed in Sec. II. A bulk polymer sample can be redrawn in a direction normal to that in which it was initially cold drawn, with resulting polymer chain orientation along the new drawing axis. In light of the model, rebuffing of a thin polymer film can be expected to turn the axis of orientation by 90° along streaks of contact between the polymer and the fibrous buffing material. Being at right angles, the new and old regions of orientation tend to compensate each other in the spatially averaged birefringence measurements. Thus, as streaks of new orientation accumulate, the net retardation will diminish until the new orientation areas constitute 50% of the surface. Magnitude of retardation will then be close to zero. Further accumulation of new streaks causes the retardation magnitude to again increase, with opposite sign. With continued buffing, the streaks of new polymer orientation begin to overlap until the whole surface of the polymer is reoriented. This sequence parallels the trajectory of the "retardation vector" in Fig. 7. The small displacement of the final points toward the right-hand side of the vertical axis can be explained as a lingering contribution from the initial orientation that is not fully reoriented by rebuffing. This contribution could be due to

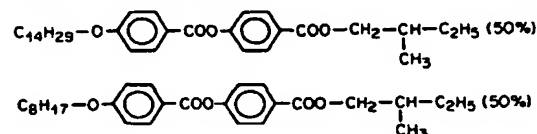
the deeper portions of the polymer layer, perhaps work hardened by the initial deformation, which fail to reorient. The net observed birefringence would be the combination of a persistent contribution in the original direction plus the contribution of the reoriented upper portion of the layer. Alignment results described in Sec. IV B suggest that the upper portion may be fully reoriented in the new direction.

IV. RELATION BETWEEN POLYMER ORIENTATION AND LIQUID-CRYSTAL ALIGNMENT

In the previous section, we have established that buffing of a thin polymer film can cause the orientation of the molecular chains of the polymer. We have also shown that such orientation occurs through a shearing deformation of the film and that this deformation accumulates in narrow streaks as buffing proceeds. We now wish to examine how some buffed polymers surfaces can interact with liquid-crystal materials to produce alignment. In the subsections below, we will discuss the aligning abilities of specific polymers, show that when alignment occurs it is caused by the oriented polymer and not by other effects such as surface scratches, and offer evidence that polymer crystallinity is necessary for alignment to occur. Finally, we will propose the view that the aligning influence of the buffed polymer acts on the liquid crystal in a way analogous to epitaxy in solid crystal materials.

A. Alignment capabilities of the test polymers

Polymer films identical to those studied in Sec. III were spun onto pairs of indium tin oxide-coated glass plates. The polymer surfaces were buffed at a pressure of 15 g/cm² for a total distance of 40 cm on cotton cloth identical to that used previously. The pairs of plates were assembled with buffing axes parallel to form cells. The spacing was set at 5 μm by the use of glass fiber spacers. Cells were made for each of the polymers studied in Sec. IV and each were tested for its ability to align both a smectic and a nematic mixture. The smectic mixture was composed of two chiral esters synthesized^{10,11} by Goodby:



This material exhibits the isotropic-to-smectic-A phase sequence with transition temperature of 56 °C. It was selected because of its room-temperature smectic-A range and because the isotropic-to-smectic-A transition is especially favorable for producing alignment. The nematic was the commercial mixture E80, manufactured by BDH, with an isotropic-to-nematic transition at 60 °. The cells were filled in the isotropic state and cooled. Texture formation was observed by polarized light microscopy as cooling proceeded. Experience with other materials has shown that alignment results do not vary dramatically from one nematic or smectic to another and the results with these two materials were taken as typical of each class of material.

The results of the alignment tests are summarized in Table II. The polymers fall into two broad categories. Those

TABLE II. Alignment obtained with various buffed polymer films.

Polymer	Smectics		Nematics	
	Aligns	No alignment	Aligns without defects, sheet nucleation	Aligns with defects, point nucleation
Polyethylene-terephthalate	×		×	
Nylon 6/6	×		×	
Polyvinyl alcohol	×		×	
Polyformaldehyde		×		×
Polystyrene		×		×
Polycarbonate		×		×
Polymethylmethacrylate		×		×
Bare glass		×		×

listed first in the table seem to exert a strong aligning influence. They are the only ones of the polymers that align the smectic material at all. As the cell is cooled, nucleation of aligned smectic-*A* material is observed to occur in numerous elongated patches which grow until they fill the cell. With polymers of the second category, the smectic-*A* phase nucleates at numerous tiny points and grows out into the cell along a different axis of alignment from each point, with no discernable preference for the buffing direction. With the nematic material, alignment of some quality is observed for all the polymers. However, with polymers of the first category, "sheet nucleation" on the cell surfaces is observed as the nematic phase is entered. These nematic layers grow in thickness until they meet in the center of the cell, producing a flaw-free aligned texture. With polymers of the second category, the nematic phase nucleates in numerous isolated spots whose alignment is either random or is only loosely correlated with the buffing axis. As the spots grow and join, their alignment axes change and become oriented parallel to the buffing axis. Disclinations generally remain, disrupting the alignment. Thus, although an aligned texture is attained, the aligning influence exerted by polymers of the second category on nematics is of a weaker kind than that exerted by polymers of the first category.

Additional cells were fabricated, buffed like the others, but lacking any polymer coating. They were found to align the nematic material like the cells with surface coatings of the second-category polymers. This implies that the second-category polymers exert no aligning influence of their own and that their relatively weak aligning abilities are due to other effects of buffing. These cells were incapable of producing any alignment of the smectic material and thus again resembled the cells with second-category coatings. These results, together with those of the previous paragraph, indicate that only polymers of the first category are capable of exerting an aligning influence of their own, over and above the influence of buffing itself in the absence of any polymer coating. Hence, only polymers of the first category seem capable of "polymer alignment," with second-category polymers showing no behavior substantially different from an uncoated cell surface.

Examining the properties of the two categories of polymers, the distinction between the two categories becomes

evident: those of the first category are highly crystalline materials, while those of the second category are strongly amorphous. The only exception is polyformaldehyde, which is highly crystalline, yet caused no alignment of the smectic material and caused only the weaker form of alignment in the nematic material. As reported in Sec. III, this polymer exhibited complete relaxation of buffing-inducing birefringence at 40 °C and some relaxation could even be seen at room temperature as the retardation measurements were being made. Since the cells were filled at temperatures above the clearing points (56 and 60 °C) of the test materials, the polyformaldehyde coating should have been fully relaxed and thus should have not caused alignment. Thus, the differences in alignment ability of the two categories of polymer seem to correlate (in all cases where polymer orientation was retained during filling) with the crystallinity of the polymer. Consequently, both polymer chain orientation and polymer crystallinity appear to be necessary conditions for alignment, and neither is sufficient alone.

B. Alignment by bulk cold-drawn polymers

Before examining further the significance of polymer crystallinity, we would like to establish the causal link between polymer chain orientation and liquid-crystal alignment. Specifically, we want to show that the strong alignment exhibited by first-category polymers (1) can be produced by polymer chain orientation and (2) cannot be produced by other effects of the buffing process.

To establish the first point above, cells consisting of small samples of bulk cold-drawn polymer films pressed gently against a bare glass surface were fabricated. The glass surface was sprayed with 5- μ m glass fibers. Since the polymer films were somewhat warped after drawing, spacing varied greatly, but with a 5- μ m minimum. The cells were filled in the isotropic phase with both the nematic and smectic mixtures. Table III shows the polymers used and the alignment obtained. Alignment, when it occurred, was somewhat poorer in quality than obtained by buffing the thin polymer films, but could be clearly seen. Alignment is reported for the minimum thickness portions of the cells, where the best alignment was generally observed. With the smectic material, it can be seen that the results mimic sub-

TABLE III. Alignment obtained in cells made from cold-drawn polymer sheets.

Polymer	Smectics		Nematics	
	Aligns	No alignment	Aligns	No alignment
Polyethylene-terephthalate	×		×	
Nylon 6/6	×		×	
Polystyrene		×		×
Polycarbonate		×		×

stantially the alignment obtained with the same polymers in the conventional cells. The crystalline polymers align the smectic, but the amorphous polymers do not. Since the surfaces of these polymer samples were not buffed or rubbed in any way, it is clear that the observed liquid-crystal alignment must have been a consequence of polymer orientation alone. With the nematic material, alignment can again only be obtained with the crystalline polymers.

The above results show that chain alignment of crystalline polymers is clearly capable of causing alignment in the complete absence of any buffing. We now need to demonstrate that other consequences of buffing are not capable of producing the alignment results that the crystalline polymers are able to produce. The prime candidate for such an effect is the formation of very fine mechanical scratches or grooves on the polymer surface by the buffing process. However, all of the polymers tested should be liable to such surface damage. Yet none of the amorphous materials could exert an aligning effect any stronger than that resulting from the buffing or a bare cell surface. Thus, it appears that, even if scratching or grooving occur, they are incapable by themselves of producing the observed alignment. This was confirmed by an experiment in which a cell was assembled using surfaces that had been buffed and then rebuffed at a 90° angle to the initial buffing direction, like the sample presented in Fig. 7. The polymer used was polyethyleneterephthalate, the buffing distance was 40 cm for both buffs, and the cell spacing was 5 μm . With both smectic and nematic alignment, it was found that the effect of the initial buff was fully overwhelmed by the second one, so that the liquid-crystal molecules were now parallel with the direction of the second buff. If the alignment were caused by scratching, one would expect a fine network of criss-crossing scratches to be produced which would be ineffective at producing a good aligned texture.

C. Polymer alignment as a form of epitaxy

The evidence presented in the above section makes it clear that chain orientation in crystalline polymers is responsible for the strong alignment that those polymers produce. We now want to address briefly the question of how such polymers interact with liquid-crystal materials to cause alignment. Liquid crystals, as their name implies, share some of the properties of conventional solid crystals. In polymer alignment, when the liquid-crystal phase begins to form from the isotropic, it nucleates on the polymer surfaces (ei-

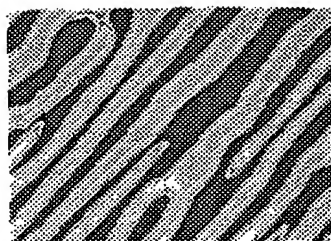


FIG. 8. Micrograph of partially formed smectic texture.

ther as a sheet as with nematics or in elongated patches as with smectics) and grows out into the bulk of the cell. Thus, the formation of one "crystalline" material, the liquid-crystal phase, has been initiated on the surface of another crystalline material, the oriented polymer, and at least one crystal property, the direction of the molecular axes, has been preserved from one material into another. To this extent, the alignment process resembles epitaxy of conventional solid crystals. Of course, in solids very exact conditions of lattice match generally must be met for epitaxy to occur. But with liquid crystals it is plausible that their much less rigid crystal order would make them much more accommodating of mismatch between substrate and "epi." The liquid-crystal molecules would see the crystalline substrate as resembling an already formed liquid-crystal phase and act as though extending that phase further in space.

Observation of the transition from isotropic to aligned smectic *A* tends to support the above picture. Figure 8 shows a 9- μm -thick glass cell with rubbed PET on one face and polystyrene on the other. The cell was filled with the second of the two ester materials described above. The micrograph was taken between crossed polarizers. The black areas are portions of the cell where all of the material is isotropic. The light areas are aligned smectic *A* (with the rub axis at 45° to the polarizer axis), showing the streaked appearance that is typically observed during *A*-phase formation with polymer alignment. The birefringence of the aligned material gives rise to light and dark bands around the borders of the streaks that map out the thickness of the smectic material. Visual examination of the sample's behavior as the smectic texture forms indicate that the material is thin at the edges of the streaks and becomes thicker in the center, where it eventually touches the opposite face of the cell. The uniform gray areas in the interior portions of the streaks are the areas of contact.

Figure 9 shows qualitatively a cross-section view of the cell deduced from micrographs like that of Fig. 8. It can be

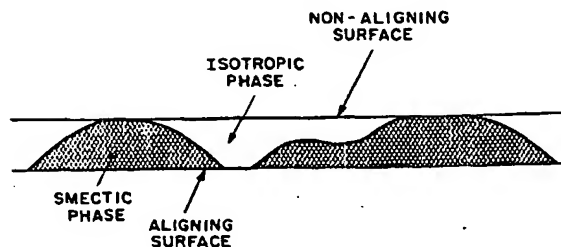


FIG. 9. Typical qualitative cross-section view of cell during formation of smectic texture, as deduced from observation of birefringent contours.

seen that the smectic material preferentially wets the aligning surface relative to the isotropic material. The polystyrene-coated surface shows just the opposite behavior and is wetted preferentially by the isotropic material relative to the smectic material. Since it is generally true that substances that wet each other tend to be similar, these wetting affinities suggest that the isotropic material bears a resemblance to the polystyrene surface, and that the smectic material bears a resemblance to the aligning surface. This makes sense in light of the epitaxy analogy which suggests that the smectic and aligning surface are alike in their being crystalline. The wetting affinity of the isotropic material and the polystyrene surface also make sense since these materials are alike in their being amorphous and noncrystalline.

- ¹J. S. Patel, T. J. Leslie, and J. W. Goodby, *Ferroelectrics* **59** 137 (1984).
- ²J. Cognard, "Alignment of Nematic Liquid Crystals and Their Mixtures," *Mol. Cryst. Liq. Cryst.* **51**, 1 (1982).
- ³D. W. Berreman, *Phys. Rev. Lett.* **28**, 1683 (1972).
- ⁴D. W. Berreman, *Mol. Cryst. Liq. Cryst.* **23**, 215 (1973).
- ⁵J. A. Castellano, *Mol. Cryst. Liq. Cryst.* **94**, 33 (1983).
- ⁶K. Kondo, H. Takezoe, A. Fukuda, and E. Kuze, *Jpn. J. Appl. Phys.* **22**, L85 (1983).
- ⁷H. Aoyama, Y. Yamazaki, N. Matsuura, H. Mada, and S. Kobayashi, *Mol. Cryst. Liq. Cryst.* **72**, 127 (1981).
- ⁸M. E. Becker, R. A. Kilian, B. B. Kasmowski, and D. A. Mlynski, *Mol. Cryst. Liq. Cryst.* **132**, 167 (1986).
- ⁹N. A. Clark, *Phys. Rev. Lett.* **55**, 292 (1985).
- ¹⁰J. W. Goodby and T. M. Leslie, *Liquid Crystals and Ordered Fluids*, edited by A. C. Griffin and J. F. Johnson (Plenum, New York, 1984), Vol. 4, p. 1.
- ¹¹J. W. Goodby and T. M. Leslie, *Mol. Cryst. Liq. Cryst.* **110**, 175 (1980).

Effect of the Polymer Tilt Angle for Generation of Pretilt Angle in Nematic Liquid Crystal on Rubbed Polyimide Surfaces

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We have studied the effect of the polymer tilt angle for pretilt angle generation in nematic liquid crystal, 4-cyano-4'-n-pentylbiphenyl (5CB) on rubbed polyimide surfaces. The polymer tilt angle was determined by measuring induced optical retardation produced in rubbed polyimide (PI) surfaces by rubbing. We suggest that the polymer tilt angle is not related directly to the pretilt angle on rubbed PI surfaces by rubbing. We proposed a microscopic model of pretilt angle generation on rubbed PI surfaces by rubbing. Finally, we conclude that the pretilt angle generation of 5CB strongly depends on the characterization of polymer materials and the micro-asymmetric triangular structure of the polymer on rubbed polyimide surfaces.

KEYWORDS: polymer tilt angle, pretilt angle, nematic liquid crystal, polyimide, optical retardation

1. Introduction

Uniform alignment of liquid crystals (LCs) on treated substrate surfaces is very important for both LC fundamental research and applications.¹⁾ Among the LCs surface alignment techniques, the rubbing method has been most widely used, however detailed mechanism of LC alignment on rubbed PI surfaces is not yet fully understood. In the surface alignment of LCs to prepare an LC cell, it is necessary to generate pretilt angle in a cell in order to avoid the creation of disclinations. The pretilt angle is also important matter in order to avoid the stripe domain on super twisted nematic liquid crystal displays (STN-LCD)²⁾ and surface-stabilized ferroelectric liquid crystal display (SSFLCD).³⁾ The generation of pretilt angle in nematic liquid crystals (NLCs) on alignment layers by unidirectional rubbing was demonstrated and discussed by many investigators.^{4–12)}

Recently, we reported the aligning capabilities of the NLC, 5CB, on rubbed PI,^{7–12)} polypyrrole (PP),¹³⁾ PI Langmuir-Blodgett (LB),¹⁴⁾ polystyrene (PS),¹⁵⁾ and PI containing trifluoromethyl moieties.¹⁰⁾ Geary *et al.* reported the orientation of polymers for LC alignment on various alignment layers by the rubbing process.⁵⁾ Recently, Han *et al.* reported the relationship between the polymer tilt angle and the pretilt angle in NLC on rubbed PI surfaces by rubbing.¹⁶⁾

In this paper, we report the effects of the polymer tilt angle for generation of pretilt angle in 5CB on various rubbed PI surfaces by rubbing.

2. Experimental

The PI materials, studied were:

RN-626 (PI, Nissan Chemical Industries Co., Ltd.)

: Containing trifluoromethyl moiety and low polarization.

SE-150 (PI, Nissan Chemical Industries Co., Ltd.)

: With side chain and medium polarization.

RN-305 (PI, Nissan Chemical Industries Co., Ltd.)

: Without side chain and highest polarization.

The precursors were coated on indium-tin-oxide (ITO)-coated glass substrates, and imidized at 250°C for one hour. The PI films were rubbed using a machine equipped with a nylon roller (Y_o-15-N, Yoshikawa Chemical Industries Co., Ltd.). The definition of the rubbing strength, *RS*, was given in previous papers^{8–10)} The LC was assembled in cells with antiparallel-rubbed surfaces. The polymer tilt angle was defined by measuring the optical retardation measurement system as shown in Fig. 1. The light source is a He-Ne laser (632.8 nm) with 2 mW output, an acoustic modulator, and an analyzer and the output signal is detected by a photodiode. We defined that the polymer tilt angle is symmetric point of optical retardation for 0 deg of angle of incidence on rubbed surfaces. The pretilt angle of the LC media in the nematic phase were measured using the crystal rotation method.¹⁷⁾

3. Result and Discussion

Figure 2(a) shows the induced optical retardation (after rubbing value-bare ITO value) of the rubbed PI surface (SE-150) as a function of angle of incidence by rubbing. The polymer tilt angle is 0 for *RS*=0, but the polymer tilt angle increases with the *RS*. Figure 2(b) shows the induced optical retardation (after rubbing value-bare ITO value) of the rubbed PI surface (RN-305) as a function of angle of incidence by rubbing. The polymer tilt angle is about 0 for all *RS*. Figure 3 shows the polymer tilt angle on three kinds of the rubbed PI surfaces as a function of *RS*. It is shown that the polymer tilt angle is 0 for all *RS*=0 on three kinds of PI surfaces. We consider that the polymer tilt angle is parallel for unrubbed PI surfaces. The polymer tilt angle increases with the *RS*, on PI surfaces (SE-150 and RN-626) but does not increase on PI surface (RN-305)

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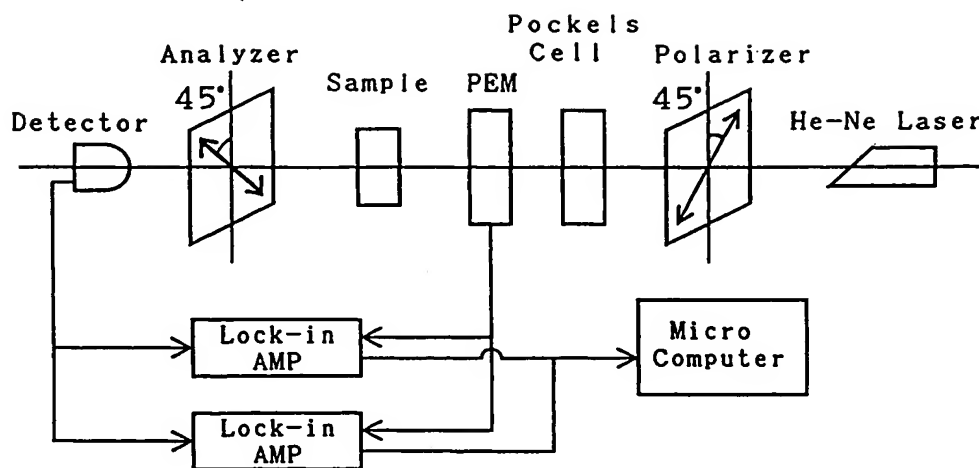


Fig. 1. The measurement system of the optical retardation.

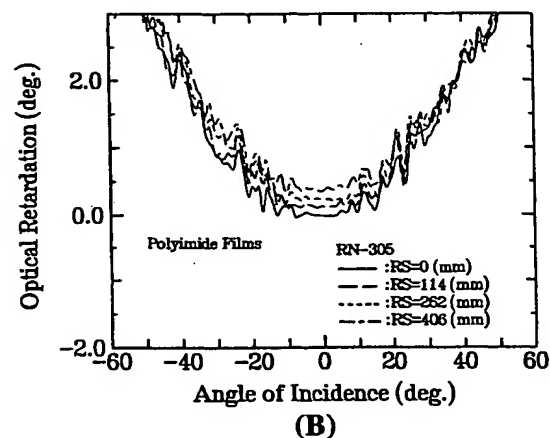
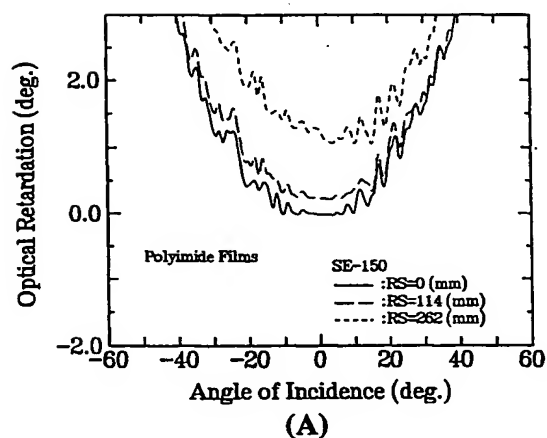
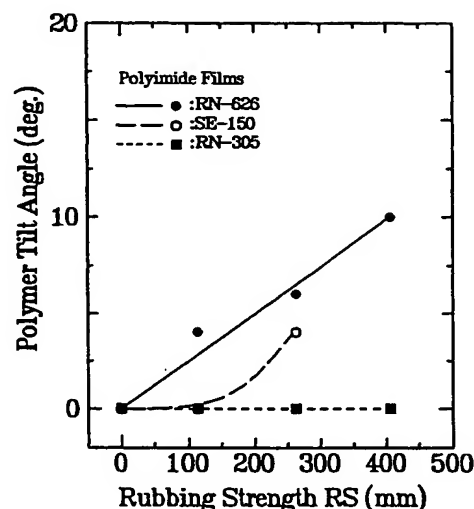
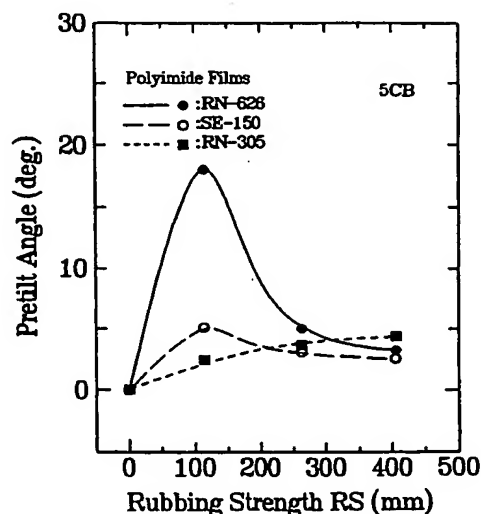


Fig. 2. Induced optical retardation produced in rubbed PI surfaces as a function of angle of incidence. PI are (a) SE-150; (B) RN-305.

with the *RS*. From these results, we suggest that the polymer tilt angle strongly depends on the polymer materials.¹⁸⁾ We consider that the polymer tilt angle on rubbed PI surface indicates the easy axis of the polymer on PI surface by rubbing. Therefore, we conclude that the easy axis of the polymer on rubbed PI surfaces strongly depends on the polymer materials.

Fig. 3. The polymer tilt angle on three kinds of the rubbed PI surfaces as a function of *RS*.Fig. 4. The pretilt angle in 5CB on three kinds of the rubbed PI surfaces as a function of *RS*.

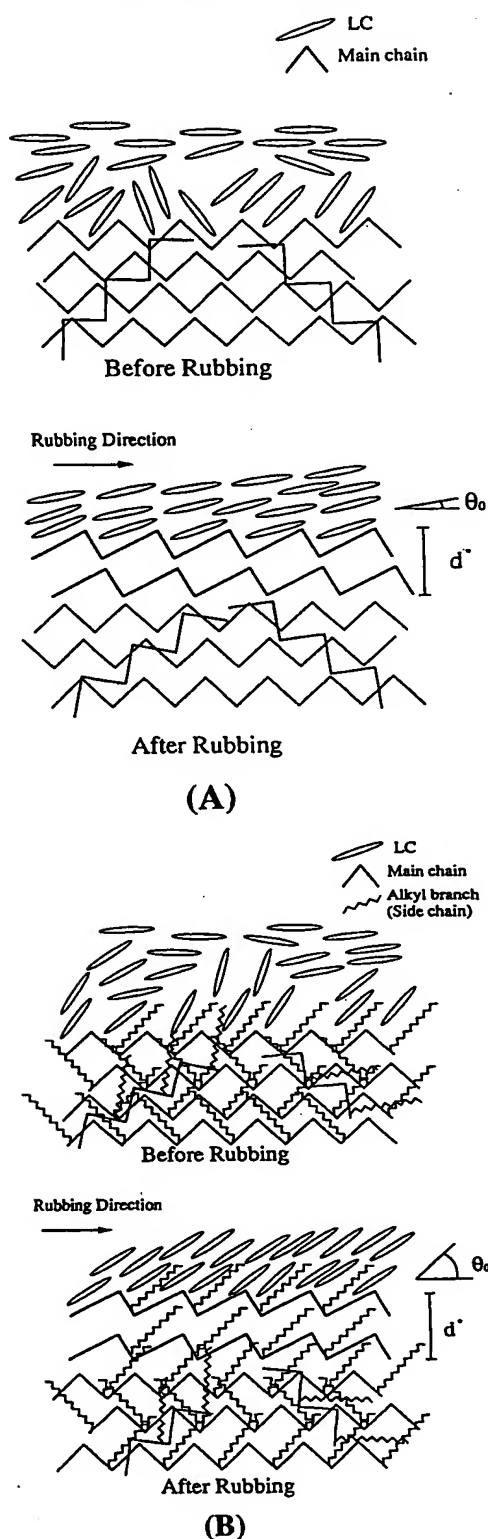


Fig. 5. The microscopic model of the pretilt angle generation on rubbed PI surfaces. (a) Without side chain; (b) With side chain.

Figure 4 shows the pretilt angle of 5CB on three kinds of the PI surfaces as a function of RS . The pretilt angle of 5CB on rubbed PI surface (RN-626) is very high for weak RS , and decreases with the RS . The pretilt angle of 5CB on rubbed PI surface (SE-150) in-

creases with the RS , and decreases with the RS . In PI surface (RN-305), the pretilt angle of 5CB increases with the RS , however, the polymer tilt angle increases with the RS for wide range of RS on PI surfaces (SE-150 and RN-626). From these results, we suggest that the polymer tilt angle is not related directly to the pretilt angle on three kinds of rubbed PI surfaces.

Figure 5 shows the microscopic model of the pretilt angle generation on rubbed PI films without side chain and with side chain. Before rubbing treatment, we consider that the PI chains show the Zig-Zag conformation, and the PI chain show the circle conformation.¹⁹⁻²⁰ After rubbing treatment, PI chain generates the expansion of the PI chain and then show asymmetric triangular structure for rubbing direction.¹⁹⁻²⁰ The pretilt angle is generated by micro-asymmetric triangular structure of the polymer on rubbed PI surface without side chain by rubbing in Fig. 5(a). In Fig. 5(b), the pretilt angle is generated by combination of the micro-asymmetric triangular structure of the polymer and the side chain on PI film having side chain by rubbing. In Fig. 5 (b), we suggest that the pretilt angle in NLC is generated by micro-surface excluded volume effect on rubbed PI film having side chain.⁷⁾

Finally, we conclude that the pretilt angle generation of 5CB strongly depends on the characterization of the polymer materials^{9,10)} and the micro-asymmetric triangular structure of the polymer on alignment-layers.

4. Conclusions

We investigated the effect of the polymer tilt angle for pretilt angle generation of the NLC aligned on three kinds of PI surfaces. That the polymer tilt angle is not related directly to pretilt angle on rubbed PI surfaces by rubbing is suggested. We proposed the microscopic model of pretilt angle generation on rubbed PI surfaces by rubbing. Finally, we conclude that the generation of pretilt angle in 5CB strongly depends on the characterization of the polymer materials and the micro-asymmetric triangular of structure of the polymer on rubbed polyimide surfaces.

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- 1) J. Cognard: *Mol. Cryst. & Liq. Cryst.* **78**, Suppl. 1 (1982) 1.
- 2) T. J. Scheffer and J. Nehring: *Appl. Phys. Lett.* **45** (1984) 1021.
- 3) N. A. Clark and S. T. Lagerwall: *Appl. Phys. Lett.* **36** (1980) 899.
- 4) M. E. Becker, R. A. Kilian, B. B. Kosmowski and D. A. Milynsky: *Mol. Cryst. & Liq. Cryst.* **130** (1986) 167.
- 5) J. M. Geary, J. W. Goodby, A. R. Kmetz and J. S. Patel: *J. Appl. Phys.* **62** (1987) 4100.

- 6) S. Kuniyasu, H. Fukuro, S. Maeda, K. Nakaya, M. Nitta, N. Ozaki and S. Kobayashi: *Jpn. J. Appl. Phys.* **27** (1988) 827.
- 7) T. Sugiyama, S. Kuniyasu, D.-S. Seo, H. Fukuro and S. Kobayashi: *Jpn. J. Appl. Phys.* **29** (1990) 2045.
- 8) D.-S. Seo, K. Muroi and S. Kobayashi: *Mol. Cryst. & Liq. Cryst.* **213** (1992) 223.
- 9) D.-S. Seo, H. Matsuda, T. Oh-ide and S. Kobayashi: *Mol. Cryst. & Liq. Cryst.* **224** (1993) 13.
- 10) D.-S. Seo, S. Kobayashi and M. Nishikawa: *Appl. Phys. Lett.* **61** (1992) 2392.
- 11) D.-S. Seo, T. Oh-ide, H. Matsuda, T. Isogami, K. Muroi, Y. Yabe and S. Kobayashi: *Mol. Cryst. & Liq. Cryst.* **231** (1993) 95.
- 12) D.-S. Seo, Y. Iimura and S. Kobayashi: *Appl. Phys. Lett.* **61** (1992) 234.
- 13) D.-S. Seo, S. Kobayashi and A. Mochizuki: *Appl. Phys. Lett.* **60** (1992) 1025.
- 14) D.-S. Seo, T. Oh-ide and S. Kobayashi: *Mol. Cryst. & Liq. Cryst.* **214** (1992) 97.
- 15) D.-S. Seo, K. Muroi, T. Isogami, H. Matsuda and S. Kobayashi: *Jpn. J. Appl. Phys.* **31** (1992) 2165.
- 16) K.-Y. Han, P. Vetter and T. Uchida: *Jpn. J. Appl. Phys.* **32** (1993) L1242.
- 17) T. J. Scheffer and J. Nehring: *J. Appl. Phys.* **48** (1977) 1783.
- 18) D.-S. Seo, K. Araya, N. Yoshida, S. Kobayashi and M. Nishikawa: *Proc. 19th Japanese Liquid Crystal Conf.* (1993) p. 110.
- 19) S. Kobayashi and Y. Iimura: *Proc. SPIE* **2175** (1994) 122.
- 20) M. Nishikawa, N. Bessho, T. Natsui, Y. Ohta, N. Yoshida, D.-S. Seo, Y. Iimura and S. Kobayashi: submitted to *Mol. Cryst. & Liq. Cryst.* (1994).